



activities

# Newsletter

of the International Global Atmospheric Chemistry Project

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## A Note From the IGAC Co-Chairs: Mary Scholes and Tim Bates

### Towards a Second Phase of IGAC

The past decade of research within the International Global Atmospheric Chemistry (IGAC) Program has greatly increased our understanding of the chemical composition of the troposphere, the fluxes of chemical species into and out of the troposphere, and the processes controlling the transport and transformation of chemical species within the troposphere. IGAC has been particularly successful in several key areas including biosphere-atmosphere trace gas exchange (GEIA, Biomass Burning, TRAGNET), the production and reactivity of oxidizing gases (NARE, APARE, EXPRESSO, MILOPEX, BIBLE), and the chemical, physical and radiative properties of aerosols (ACE-1, TARFOX, ACE-2, ACE-ASIA) and has recently completed an integration and synthesis of its research activities [Brasseur et al., 2002 in press].

Perhaps as importantly, IGAC has brought together the atmospheric and biospheric research communities over the past several years. The remote sensing community, atmospheric modeling community, and gas and aerosol in-situ measurement communities are now working side-by-side in the field and in data workshops to better understand the chemistry of the atmosphere. The synergy and momentum from IGAC-I provide a good foundation on which to build a new Atmospheric Project (IGAC-II) under IGBP Phase II.

IGBP Phase II is focusing research at the Earth System level by bringing together scientists from across traditional boundaries. Understanding the Earth's systemic behaviour and the effects and feedbacks due to human perturbations clearly require this interdisciplinary research approach. While there are still many areas of atmospheric chemistry where advances can be within the discipline, an understanding of the functioning of the Earth System will only be achieved if scientists are encouraged to cross disciplinary boundaries and work together in common research directions.

Discussions of future research directions for IGAC have taken place at two sessions of the IGAC Scientific Conference in Bologna, Italy in 1999, a one-day discussion led by the IAMAS Commission on Atmospheric Chemistry and Global Pollution (CACGP) that was held at the IGAC Integration and Synthesis Meeting in Aspen, USA in 2000, and a workshop in Stockholm, Sweden in January 2002. The science

features in this issue of IGACtivities were overview presentations at the Stockholm workshop. In March 2002 the IGAC SSC spent two days discussing future research directions during their meeting in the Kruger National Park, South Africa. Several key themes have emerged from this series of discussions that effect issues of climate and air quality over large regional and global scales:

## **1. What is the role of atmospheric chemistry in amplifying or damping climate change?**

- How will changing emissions and depositions of gases affect spatial patterns of climate forcing?
- What are the relative roles of stratosphere-troposphere exchange, anthropogenic and natural precursor emissions, and *in situ* photochemical processes in controlling O<sub>3</sub> and its effect on global change?
- What are the sources, sinks, distributions and properties of aerosols and their direct radiative effects on climate?
- What are the effects of aerosols on clouds, their optical properties, precipitation, and regional hydrologic cycles?
- How will a changing climate affect the chemical composition of the atmosphere?

## **2. Within the Earth System, what effects do changing regional emissions and depositions, long-range transport, and transformations have on tropospheric chemical composition and air quality?**

- What are the export fluxes of oxidants, aerosols, and their precursors from continents (e.g., megacities, biomass burning, desert dust) to the global atmosphere?
- What are the impacts of intercontinental transport on surface air quality?
- How will human activities transform the dynamical and chemical properties of the future atmosphere?

International coordination and collaboration are essential to address these global scientific questions. The required research efforts encompass three fundamental objectives that IGAC-II will pursue:

- *To accurately determine global distributions of both short and long lived chemical species in the atmosphere and to document their changing concentrations over time.*
- *To provide a fundamental understanding of the processes that control the distributions of chemical species in the atmosphere and their impact on global change and air quality.*
- *To improve our ability to predict the chemical composition of the atmosphere over the coming decades by integrating our understanding of atmospheric processes with the response and feedbacks of the Earth System.*

This is a year of transition between IGAC-I and IGAC-II and an opportunity for us to redefine international atmospheric chemistry research priorities and establish an implementation strategy in which to accomplish our objectives. We will be contacting activity conveners soon with information on the proposed task reorganization. A draft science plan will be written this summer describing the questions and objectives outlined above and will be posted on the web before the Science Symposium in September. We hope you will join us on the afternoon of September 18, 2002 in Crete to discuss the plan and future of IGAC. We welcome your comments and suggestions.

## Interactions between anthropogenic aerosols and the hydrologic cycle

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### 1. Introduction

The anthropogenic component of sulfate and carbonaceous aerosols has substantially increased the global mean aerosol burden from pre-industrial times to the present-day and can influence the climate in different ways. The direct aerosol effect is caused by the absorption and scattering of solar radiation (see Boucher, this issue). Additionally, aerosols act as cloud condensation nuclei and thereby determine the initial cloud droplet number concentration, albedo, precipitation formation, and lifetime of warm clouds. For a constant liquid water path, an enhancement in the cloud droplet number leads to an increase in cloud albedo (cloud albedo or first indirect aerosol effect). As smaller cloud droplets have a lesser chance to collide and form precipitation size drops, the enhancement in cloud droplet number and decrease in cloud droplet size due to anthropogenic aerosols may cause a reduction in precipitation formation and increase cloud lifetime (cloud lifetime or second indirect aerosol effect). The cooling of the cloud albedo effect is estimated to be between 0 and  $-2 \text{ W m}^{-2}$  in the global mean, but is still very uncertain [Ramaswamy *et al.* 2001]. The cloud lifetime effect is not a forcing because it involves interactions of aerosols with cloud droplets. It is estimated to be of comparable magnitude to the cloud albedo effect. This effect is even more uncertain because changes in the hydrologic cycle associated with aerosols presently cannot be deduced from observational studies alone, but depend on a modeling component to fill in the gaps. It is these latter interactions between aerosols and the hydrologic cycle that will be discussed below.

### 2. Observational evidence for aerosol effects on the hydrologic cycle

In recent years observational evidence for the cloud lifetime effect has been obtained. Brenguier *et al.* [2000] measured cloud microphysical properties with 5 instrumented aircraft and remotely measured cloud radiative properties with a lidar and radiometers during the second Aerosol Characterization Experiment (ACE-2). ACE-2 took place between Portugal and the Canary Islands in June-July 1997. The simultaneity of the measurements

enabled the authors to provide for the first time observational evidence of both the first and second indirect effect in boundary layer clouds forming in polluted continental outbreaks.

Analyzing cloud microphysical measurements over the North Atlantic and the Arctic [Peng *et al.* 2002] showed that polluted clouds, characterized as clouds in which the accumulation mode aerosol number concentration below cloud base exceeded  $300 \text{ cm}^{-3}$ , have far less drizzle size drops than clean clouds adding further evidence for the cloud lifetime effect. Similar conclusions were reached from data analyzed from the Monterey Area Ship Track study (MAST) by [Ferek *et al.* 2000]. They concluded that although drizzle was a relatively infrequent occurrence during MAST, diverse measurements from several sources produced data signals consistent with a reduction in drizzle drops in stratus clouds affected by ship effluents. Concurrent increases in liquid water in the cloud droplet size range, due to redistribution from the drizzle mode, were not always observed. This is possibly because of the relatively small and often negligible amounts of water in the drizzle mode.

Ramanathan *et al.* [2001] assembled polluted and clean clouds from aircraft measurements in different climatic regimes (Indian Ocean, Australia, Amazon basin) and evaluated the cloud droplet effective radius (ratio of the third to the second moment of the cloud droplet size distribution) as a function of cloud temperature which can also be interpreted as height above cloud base. The clean clouds systematically had effective radii exceeding  $14 \mu\text{m}$ , the threshold for drizzle formation. In polluted clouds this threshold effective radius was only exceeded if the cloud temperature dropped below  $-10^\circ\text{C}$  suggesting that the cloud may have started to glaciate in its upper part. Otherwise these polluted clouds had smaller effective radii as expected if the cloud water content is distributed over more cloud droplets.

Rosenfeld *et al.* [2001] re-evaluated the correlation between increasing dust frequency and decreasing rainfall in the Sahelian region. In light of the above findings, they concluded that the increased dust frequency may not be the result of decreased precipitation. Instead, because dust aerosols also act as cloud condensation nuclei, the increased dust frequency may be the cause of decreased precipitation due to the cloud lifetime effect. Breon *et al.* [2002] derived aerosol concentration and cloud droplet radii from 8 months of measurements from the POLDER satellite to explore the effect of aerosol on cloud microphysics. They determined that cloud droplet size decreases with increasing aerosol index which is representative of the aerosol column number. This shows that the effect of aerosols on cloud microphysics is significant and occurs on a global scale.

### 3. Can anthropogenic aerosol emissions in the Northern Hemisphere influence the precipitation in the Tropics ?

A mechanism by which anthropogenic aerosols could influence the Sahelian rainfall was proposed by Rotstajn and Lohmann [2002] and Feichter *et al.* [2002]. They used different atmospheric general circulation models (GCM), the CSIRO and ECHAM4 GCM, respectively, coupled to a mixed layer ocean to conduct equilibrium experiments in response to the anthropogenic aerosol loading. Whereas Rotstajn and Lohmann [2002] only included sulfate aerosols, Feichter *et al.* [2002] considered sulfate, dust, sea-salt and carbonaceous aerosols. In both simulations the greenhouse gas concentrations were kept at present day values. In the pre-industrial simulations, the fossil fuel emissions were set to zero and the biomass burning emissions were reduced to 0% or 10% of their present-day values. The CSIRO model only considers the cloud albedo and the cloud lifetime effect by empirically relating the sulfate aerosol mass to the number of cloud droplets. In this approach sulfate aerosols are used as a surrogate for all aerosols.

The ECHAM model considers the direct and the semi-direct aerosol effect in addition to both indirect aerosol effects. The semi-direct effect is referred to absorption of solar radiation by black carbon which can lead to a heating of the air and can result in an evaporation of cloud droplets. Thus, the warming caused by the semi-direct effect can partially offset the cooling due to the indirect aerosol effect, as outlined in Lohmann and Feichter [2001]. Here the number of cloud droplets is obtained from a balance equation. Cloud droplet nucleation is parameterized as a function of total aerosol number concentration, updraft velocity, and a shape parameter, which takes the aerosol composition and size distribution into account. The total number of aerosol particles is obtained as the sum of marine sulfate aerosols produced from dimethyl sulfide, hydrophilic organic and black carbon, submicron dust, and sea-salt aerosols. Anthropogenic sulfate aerosols only add mass to the pre-existing aero-

sols but do not form new particles.

The response due to the anthropogenic aerosol loading in both models was then obtained as the difference between the present-day and the pre-industrial simulations. The surface temperature was reduced everywhere caused by the different anthropogenic aerosol effects. As this cooling is largest in the Northern Hemisphere, it changes, for instance, the meridional gradient of the sea surface temperature in the Atlantic. In the model simulations, this strengthens the trade winds and reduces the strength of the African monsoon resulting in drought conditions in the Sahelian region.

The strength of the African monsoon and the observed rainfall amounts in the Sahelian region closely follow the trends in sulfur dioxide emissions. The Sahelian precipitation decreased continuously from the 1950s through the 1980s but recovered in the 1990s. This coincides with reduced emissions of sulfur dioxide enforced by the Clear Air Act in North America in the 1980s and in Europe in the 1990s.

Rotstajn and Lohmann [2002] compared the hemispheric difference in cloud droplet effective radius from the model to satellite estimates. The underlying idea is that the higher aerosol concentrations in the Northern Hemisphere caused by anthropogenic activity would lead to more but smaller

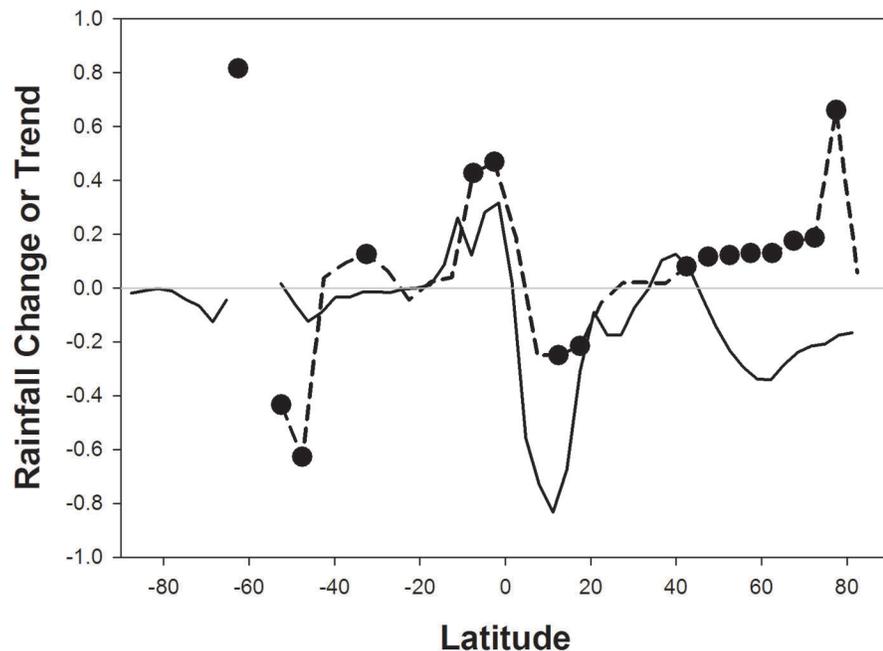


Figure 1. The zonally averaged trend in observed annual-mean precipitation [ $\text{mm day}^{-1} \text{ century}^{-1}$ ] over the period 1901 to 1998 (dashed line) and the zonally averaged difference in annual-mean precipitation [ $\text{mm day}^{-1}$ ] between present-day and pre-industrial simulations with the CSIRO GCM (solid line). The points at which the observed trend is significant at the 5% level are presented as black circles.

cloud droplets so that the cloud droplet size distribution is characterized by a smaller effective radius. Unfortunately, the two available satellite retrievals by Han *et al.* [1994] and Kawamoto *et al.* [2001] substantially differ in their estimates of the hemispheric effective radius difference over the oceans. Whereas Han *et al.* [1994] predict 0.9  $\mu\text{m}$  smaller droplets in the North Atlantic, Kawamoto *et al.* [2001] actually predict 0.1  $\mu\text{m}$  larger droplets over the North Atlantic as compared to the South Atlantic. The CSIRO models agrees exactly with the earlier estimate by Han *et al.* [1994].

The change in zonally averaged rainfall in response to the anthropogenic aerosol loading from the CSIRO model is shown in Figure 1 together with the observed trend in precipitation from 1901 to 1998. Most striking is the southward shift in precipitation with a decrease between the equator and 20° N and an increase between 20° S and the equator in both the model and the observations. The increase in precipitation in the Northern Hemisphere mid latitudes probably results from the increase in greenhouse gases and, therefore, cannot be captured in this simulation where greenhouse gas concentrations were kept constant. The ECHAM model gives similar results (not shown). Here the shift in precipitation is less pronounced because of the effect of including biomass burning aerosols that cool the tropical southern hemisphere and therefore reduce the meridional temperature gradient in the Atlantic if compared to including only the effect of sulfate aerosols.

Analyses in more detail, in agreement with observations, show that both models simulate less precipitation over the Sahel zone in response to a weaker summer monsoon. In other words, the authors suggest that the simultaneous increase in the abundance of atmospheric greenhouse gases and aerosol particles since World War II may have contributed to the observed drought in Western Africa via a change in the meridional temperature gradient. The increase in sulphate aerosols over the North Atlantic results primarily from fossil fuel use in North America and Europe. Control of sulphur emissions in the industrialized countries of the northern hemisphere might have been a significant factor in the recovery from the drought during the 1990s. If confirmed, this hypothesis would provide a striking example of a teleconnection between anthropogenic perturbations in the industrialized regions of the northern mid-latitudes and climate change in the subtropics.

#### 4. Can anthropogenic aerosols influence mid-latitude precipitation?

Since natural ice nuclei are scarce especially at small supercoolings, on the order of 1 ice nuclei in 1 million aerosol particles, anthropogenic ice nuclei can potentially be a very important contributor to glaciation of supercooled clouds. However, the connection between aerosols and ice clouds is presently considered to be too uncertain to even

speculate on whether it would be a positive or negative radiative climate forcing [Ramaswamy *et al.* 2001].

Evidence for ice-forming activity of soot particles of various sizes as contact nuclei has recently been studied in a cloud chamber for temperatures ranging from -5°C to -20° C [Gorbunov *et al.* 2001]. They found that the fraction of soot particles forming ice crystals increased with decreasing temperature, increasing size of the aerosol particles and with the degree of oxidation of the soot particle surface. If soot was oxidized, the surface chemical groups could form hydrogen bonds with water molecules.

These findings motivated Lohmann [2002] to propose the hypothesis that anthropogenic soot aerosols can influence the glaciation of clouds and with that modulate the indirect aerosol effect as shown in Figure 2. If no ice nuclei are present, more aerosols lead to more cloud condensation nuclei (CCN), a higher cloud droplet number concentration (CDNC) and less precipitation. For a constant liquid water content, this will increase cloud albedo. In addition, the reduction in precipitation prolongs the lifetime of clouds and the cloud fraction, which also increases the cloud albedo.

If, on the other hand, sufficient contact ice nuclei (IN) are present, more ice particles (IP) can be formed. This would lead to more frequent glaciation of supercooled clouds as the ice crystals grow rapidly at the expense of the droplets in a high ice supersaturated environment so that more precipitation is formed. As a consequence, the cloud fraction would decrease thus allowing more shortwave radiation to be absorbed in the Earth-atmosphere system.

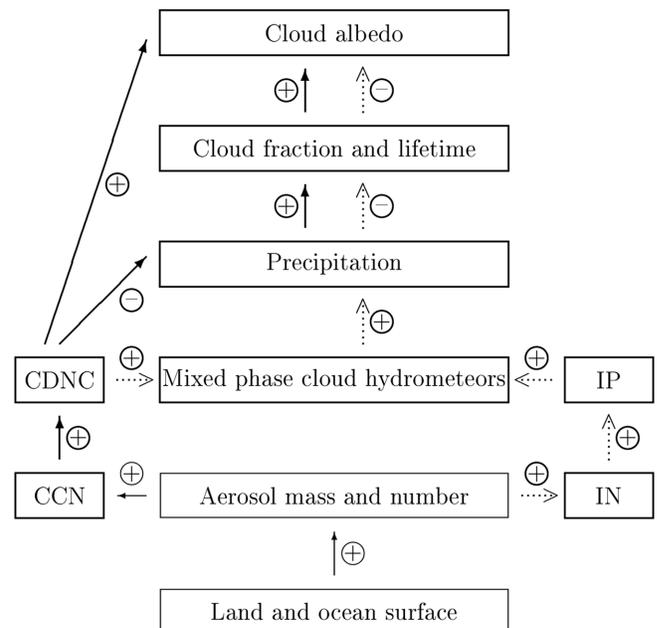


Figure 2. Schematic diagram of the warm indirect aerosol effect (solid arrows) and glaciation indirect aerosol effect (dotted arrows).

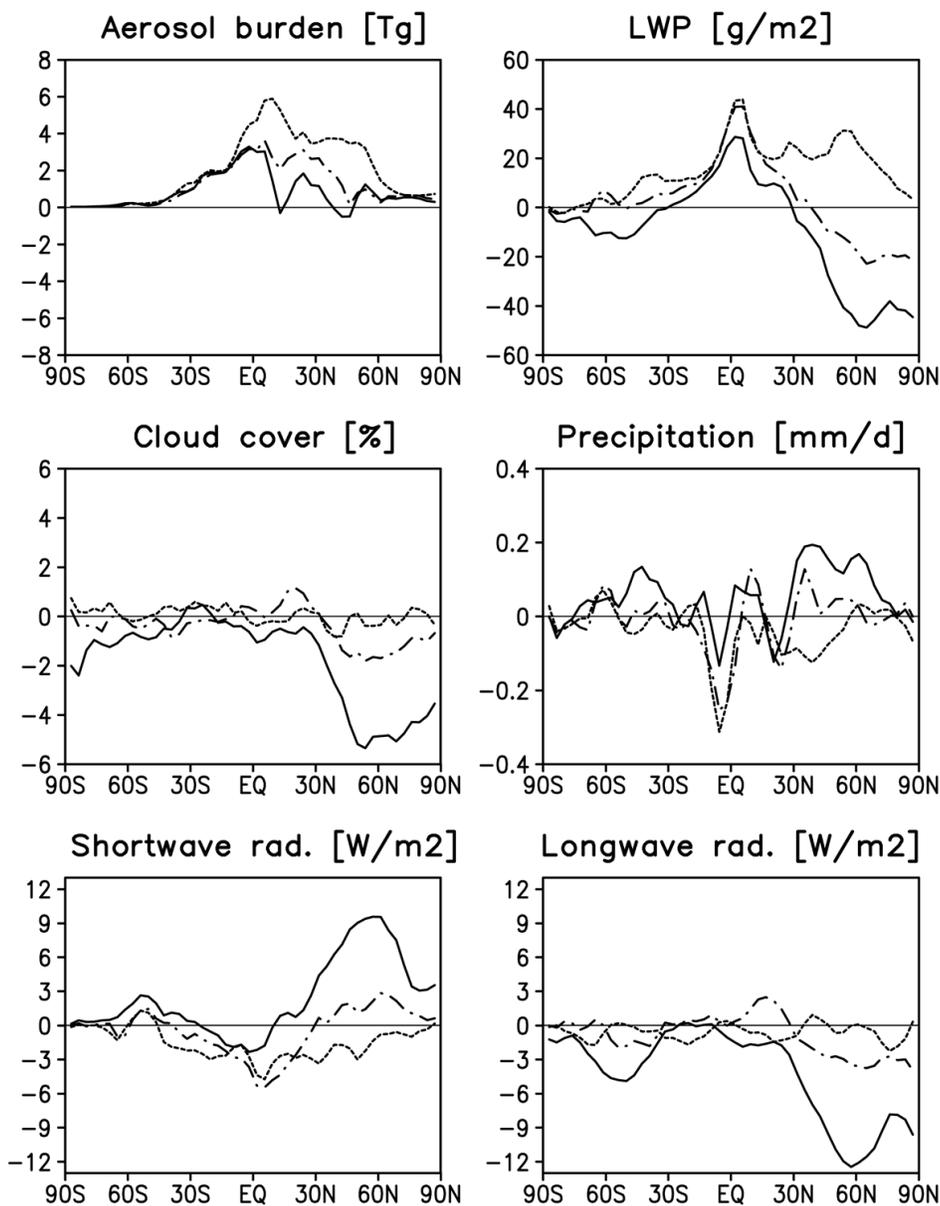


Figure 3. Zonal annual mean changes between present-day and pre-industrial times as a function of latitude. Simulations are presented with 10% black carbon (solid black line), 1% black carbon (dot-dashed line), and no black carbon (dotted line).

Sensitivity studies with varying amounts of soot acting as ice nuclei showed that if 1% to 10% of the hydrophilic black carbon acted as ice nuclei in addition to dust as a natural ice nuclei, then the precipitation is increased and cloud cover and liquid water path (LWP, the vertically integrated cloud liquid water amount) are decreased in mid-latitudes via the above mentioned mechanism, see Figure 3. Thus, more solar radiation can penetrate to the surface. This means, if a non-negligible fraction of soot aerosols acts as ice nuclei, the glaciation indirect aerosol effect could reverse or at least reduce the effect that anthropogenic aerosols have on the short-wave radiation at the top of the atmosphere.

## 5. Could anthropogenic aerosols change the global hydrologic cycle?

Whether aerosols scatter or absorb solar radiation, the dominant effects of aerosols on the radiation balance at the surface is a reduction in short-wave radiation. This cooling of the surface temperature leads to smaller evaporation rates which, in equilibrium, are then balanced by lower precipitation rates. This can result in a weaker monsoon due to the cooler land surface temperatures as outlined above. This will reduce the latent and sensible heat transfer from the surface to the atmosphere. To investigate the importance of this effect in a future climate Roeckner *et al.* [1999] conducted a set of transient experiment from 1860 to 2100 in which the ECHAM4 GCM was coupled to an oceanic general circulation model and included an interactive sulfur cycle. The first experiment only included carbon dioxide and other well mixed greenhouse gases (GHG), the second included GHG and the direct effect of sulfate aerosols, and the third included GHG plus tropospheric ozone and the direct and first indirect aerosol effect, the effect of aerosols on cloud albedo, empirically estimated from the

sulfate aerosol mass.

Roeckner *et al.* [1999] concluded that the hydrologic cycle will be weaker in the period (2030-50) as compared to the present-day climate when the direct and indirect effect of sulfate aerosols and tropospheric ozone are included. In this scenario, precipitation decreased by 0.4% per degree increase in temperature. In contrast, if only greenhouse gases are considered, then the precipitation increases by 0.7% / °C. The weaker hydrologic cycle in the aerosol experiment is caused by the anomalous net radiative cooling at the Earth's surface through aerosols. It is balanced by reduced turbulent transfer of both sensible and latent heat. It is interesting to note that the

direct effect of sulfate aerosols alone is not able to decrease precipitation in the warmer climate but only reduces the increase of precipitation in the warmer climate to 0.3%/°C.

## 6. Conclusions

We are entering a new area of aerosol research by investigating the interactions between aerosols and the hydrologic cycle. Research in this area started with cloud seeding research, as summarized in the overview article by Bruintjes *et al.* [1999]. Investigations in cloud seeding research are interested in satellite-based microphysical retrievals that can be combined with in situ cloud sampling to monitor the effects of natural and anthropogenic aerosol or hygroscopic seeding material on cloud droplet size evolution, and the effects of ice-forming nuclei on ice-particle concentrations, both of which determine the efficiency of precipitation production. The cloud seeding community, however, is not interested in the climate impact of anthropogenic aerosols or their effect on the global hydrologic cycle, but only the influence of aerosols on precipitation on a local to regional scale. Still, a knowledge exchange between the two research communities would be beneficial.

As presented above, increasing pollution in the Northern Hemisphere can have far reaching effects, such as contributing to droughts in the Sahel region. Such an effect could lead to positive feedbacks as a decrease in precipitation could increase dust storms and biomass burning which in turn could decrease the precipitation even more via the cloud lifetime effect. Changes in meridional sea surface temperature gradient may have further teleconnection effects that we are currently not aware of. Longitudinal changes in temperature could result from strong biomass burning and could, for instance, influence the Walker circulation. This is an area that requires further research as only recently scientists started to investigate these effects.

In general, our knowledge about aerosol effects on clouds and the hydrologic cycle is still very rudimentary. Therefore, clearly more research consisting of field experiments, laboratory studies and modeling efforts is needed in order to understand and quantify the effect of anthropogenic aerosols on clouds and the hydrologic cycle. This is especially important because cloud feedbacks in climate models still present one of the largest uncertainties. As shown in Stocker *et al.* [2001] there is still no consensus on whether clouds provide a negative or positive climate feedback in response to a doubling of carbon dioxide. It is largely because of these uncertainties in cloud feedback that the uncertainty range of the increase in the global mean surface temperature in response to a doubling of carbon dioxide varies between 1.5 and 4.5 °C.

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# Aerosol radiative forcing and related feedbacks: How do we reduce uncertainties?

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## 1. Introduction

There are now well established definitions for the climatic effects of aerosols which are split into the direct, semi-direct, first and second indirect aerosol effects. The direct effect refers to the extinction of sunlight by aerosols (as well as aerosol extinction and emission of longwave radiation), which acts primarily in clear sky. The semi-direct effect encompasses the impacts of aerosol absorption in clear (and cloudy) sky on the temperature and humidity profiles, which can feedback on cloud formation and cloud cover. The first indirect effect relates to the increase in cloud optical depth and cloud albedo due to an increase in the number and a decrease in the size of cloud droplets (for a fixed liquid water content). Finally, the second indirect effect refers to an in-

crease in the cloud liquid water content, cloud height, or cloud lifetime due to a reduced precipitation efficiency because of the decrease in the cloud droplet size. While the first and second indirect effects can be easily separated in a model framework, it may not be possible to observe them independently from each other.

The climatic effects are one among many reasons to study aerosols. It is clear from the Third Assessment Report of the Intergovernmental Panel on Climate Change that the current uncertainty on aerosol radiative forcing prevents us from a straightforward interpretation of the temperature record [Boucher and Haywood, 2001; Knutti *et al.*, 2002]. Figure 1 shows that, accounting for the uncertainties given by Ramaswamy *et al.* [2001] for the individual radiative forcings, the total aerosol radiative forcing has a much broader distribution than the total non-aerosol radiative forcing. Anthropogenic aerosols are known as an important climate agent not only affecting the Earth's temperature but also the water cycle (see contribution by U. Lohmann). Natural aerosols are part of the climate system and may be involved in climate feedbacks in a changing climate. The source of mineral dust may change following changes in the soil moisture, land use, or wind fields. The source of dimethylsulfide (a precursor of sulfate aerosols in maritime environment) may change because of a different wind field or if the oceanic food-web is changed in a warmer climate. Finally the source of sea

salt aerosol may also change if the wind field is changing. Acidic aerosols are responsible for acid deposition ("acid rain") which can be very harmful to the ecosystems. Aerosols participate to air pollution – they are usually measured as PM2.5 or PM10 – and may be responsible for human health problems. Regional to intercontinental transport of aerosols needs to be understood before designing regional policies of aerosol pollution monitoring and emission abatements. Fertilization of the world oceans occurs through deposition of aerosols; there is here a potential link between the carbon and aerosol biogeochemical cycles. Improving medium-

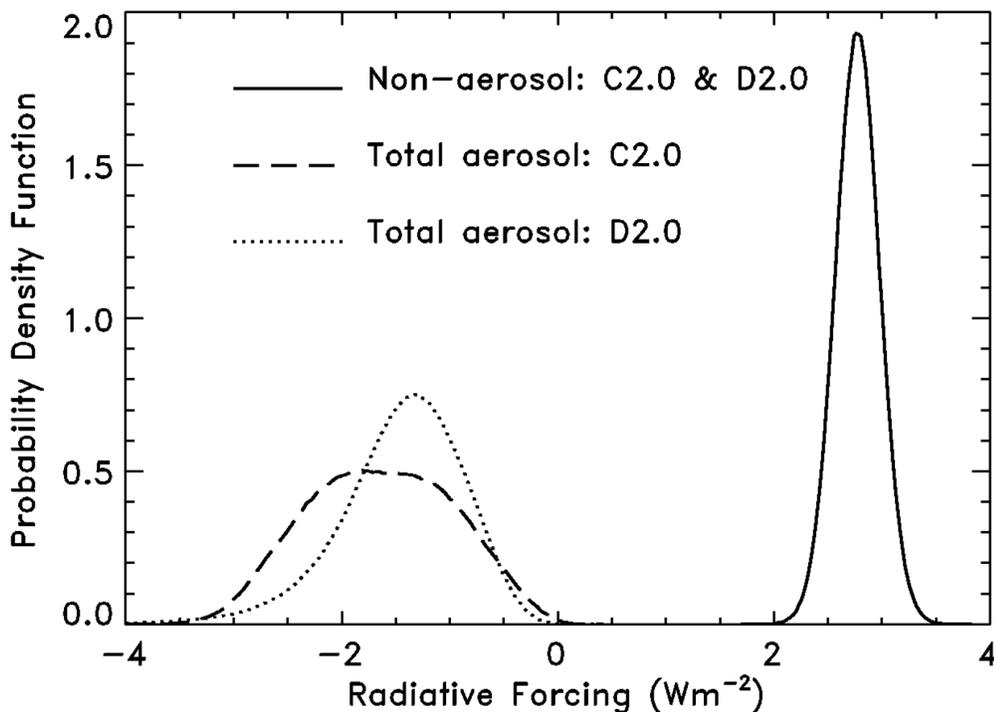


Figure 1. Probability function of the aerosol and non-aerosol radiative forcings ( $W m^{-2}$ ). The total aerosol radiative forcing has a much broader distribution than the total non-aerosol radiative forcing. This conclusion is fairly independent from the assumptions made on the exact shape of the distribution functions of the individual forcings. From Boucher and Haywood [2001].

range weather forecasts requires greater consideration of the day-to-day variability of the aerosol radiative effects and better atmospheric corrections on satellite-retrieved variables which are assimilated in numerical weather prediction models. The impacts of heterogeneous chemistry in urban to global air chemistry are still not well quantified and also deserve greater study.

In this paper, we are more particularly concerned by the direct and semi-direct effects of aerosols, the indirect effects being covered in the contributions of C. Facchini and U. Lohmann in this issue of *IGACtivities*. Our focus here is on *modeling* and *observing* aerosols at the *global scale*.

## 2. Evolution of global aerosol modeling

Global models have been used extensively to predict the global aerosol distribution and their radiative forcings. Although they include many simplifying assumptions, they remain essential tools to investigate the climatic role of aerosols. There has been considerable progress on aerosol modeling over the last 10 years (Figure 2), from the pioneering work of Langner and Rodhe [1991] to the most recent global simulations of the multi-component aerosols including sulfate, black and organic carbon aerosols from fossil fuel and biomass burning, mineral dust, and sea salt [e.g., Chin *et al.*, 2002]. Exploratory studies also simulate the contribution of ammonium and nitrate to the burden of inorganic aerosol [Adams *et al.*, 2001]. Fly ash from industrial activities may also contribute significantly to the aerosol mass in some regions [Reddy and Venkataraman, 2002; Satheesh and Ramanathan, 2000]. Aerosols were first modeled as an external mixture [e.g., Tegen *et al.*, 1997; Chin *et al.*, 2002] but progress

has been made in simulating the growth of mixed aerosol populations [Wilson *et al.*, 2001].

The direct radiative effects of aerosols depend on parameters which can be classified in 3 categories: biogeochemical parameters (such as the emission strength of the primary or secondary aerosols and the aerosol lifetime), atmospheric parameters (such as the clear-sky relative humidity, cloud cover, or surface albedo), and microphysical parameters (such as the aerosol size distribution, hygroscopicity, optical properties, and state of mixture). These 3 classes of parameters were initially treated separately, and in-situ measurements were used to prescribe the microphysical parameters not predicted by the global models. Global aerosol models are becoming able to predict the aerosol microphysical parameters, in a way that is more coherent with the rest of the physical and chemical processes [e.g., Wilson *et al.*, 2001]. This evolution in aerosol modeling has some consequences on the observational strategies needed to address the radiative effects of aerosols.

There is a large range in the simulated direct radiative forcings due to different aerosol species. The discrepancies in direct radiative forcing calculations seem to originate from the treatment of the hygroscopic and optical properties of the aerosols (as well as from the role of cloudiness in the direct aerosol effect) rather than from the aerosol burdens alone [Haywood and Boucher, 2000]. Despite the attempts of Charlson *et al.* [1992] and Penner *et al.* [2001] there does not exist a thorough budget of uncertainties of the aerosol radiative forcings. This is because the uncertainties in the individual parameters entering the calculation of the direct aerosol radiative forcing themselves are not well known. One can, for instance, raise the question of whether cloud cover uncertainty, which is mostly due to very thin cirrus clouds, is critical or not. The direct effect by aerosols may still be significant in the presence of a very thin cirrus cloud cover. Moreover, correlations among the different parameters are not well known (e.g., diurnal cycle in relative humidity, cloud cover, aerosol chemical composition, and size distribution). However, some aspects can clearly be identified as causing significant uncertainties. These include the hygroscopic properties of the mixed aerosol and the sub-grid scale distribution of relative humidity and clouds in models, the aerosol absorption (through the *spectrally-resolved* aerosol single scattering albedo), the emission strength of carbonaceous aerosols, especially in Africa and Asia, or the vertical distribution of mineral dust.

The ranges in radiative forcings given by IPCC for the aerosol direct effect are to a great extent based on the existing literature. It is hardly possible at the moment to rate the performances of the different models objectively and/or to interpret the model-to-model differences in terms of their parameterizations [Lohmann *et al.*, 2001]. There is a risk that the current spread in model results

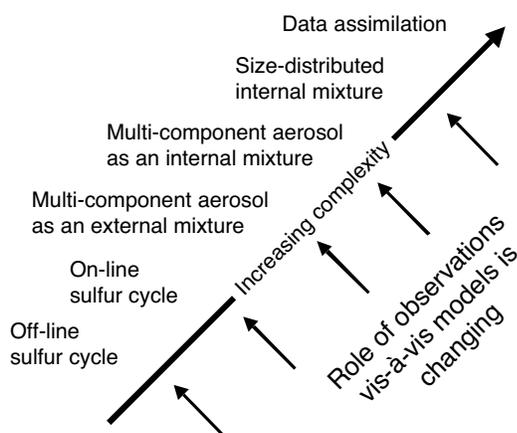


Figure 2. Schematic diagram showing the evolution of global aerosol models.

will not narrow as the models get more complex. One suggestion to solve this dilemma is to pin down and understand the model-to-model discrepancies in terms of what is causing the largest differences in aerosol radiative forcing. These aspects of the models should then be compared to observations so that eventually one can decide which model results are most reliable.

There have been few links, so far, between the urban, regional, and global scales. Different models and measurement networks are involved. Yet, mega-cities have emerged as an important research topic in atmospheric chemistry, the concerns about air pollution are rising to the regional or even hemispheric scales, and the resolution of global models is improving rapidly over time. As a consequence, it would be valuable to establish bridges between the urban and the global scales, for instance by rationalizing routine measurements. One can imagine that air pollution networks become interested in aerosol optical depth (a measurement typically made for monitoring the aerosol radiative effects) and global modelers find some interest in measurements of PM<sub>2.5</sub> concentrations averaged over large cities.

### 3. Role of observations

Clearly the role of observations vis-à-vis global-scale modeling is changing. Observations can serve many different functions.

**Evaluating Models:** Aerosol models should be evaluated with a full range of observations, including chemical, physical, and optical measurements of aerosols. Long-term continuous measurements are particularly useful to evaluate the seasonal variations in aerosol concentrations and properties in models. Particularly interesting in this context is the AERONET/AEROCAN/PHOTONS network of sunphotometers which provides measurements of aerosol optical depth as well as information on the aerosol size distribution [Holben *et al.*, 2001]. Dubovik *et al.* [2002] also analyzed these data to infer the wavelength dependence of the aerosol single scattering albedo at different locations worldwide. We are also learning much from networks set up for monitoring aerosol concentration and deposition at the regional or continental scale (such as EMEP or EMEFS). For aerosol properties more difficult to measure, and for which no monitoring is possible, compilations of existing data from field campaigns can also be very valuable. An example of this is the compilation of aerosol size distribution in the marine environment made by Heintzenberg *et al.* [2000].

**Testing Parameterizations:** Not only model results should be evaluated but also parameterizations. The most critical parameterizations in global-scale models are those of wet scavenging (in-cloud, below-cloud, or through entrainment in convective updrafts), convective transport, sub-grid scale distribution of relative humid-

ity and cloud cover. Evaluation of these parameterizations may require dedicated measurements and a hierarchy of models.

**Bridging Aerosol Knowledge Gaps:** There are still many gaps in aerosol knowledge that only innovative research can tackle. Among those gaps, one can mention i) the hygroscopic properties of the mixed aerosol (containing in particular carbonaceous species), ii) the absorption properties of the mixed aerosol (with a focus on aerosols containing black and organic carbon and dust), and iii) the formation of secondary organic aerosols. (See the contribution of C. Facchini in this issue).

**Developing Data Assimilation Schemes:** Data assimilation in global models requires data of good and uniform quality. Satellite observations with their regional or global coverage are obviously well suited for that and will be playing an increasing role in the future [Collins *et al.*, 2001]. Ground-based networks are also very interested in this respect. There is also the need for standardized continuous measurements that can easily fit in global models. T. L. Anderson suggested for instance that the accumulation to coarse mode ratio in aerosol optical depth or aerosol mass could be one such parameter.

Satellite observations of aerosols are playing an increasing role. However, aerosol remote sensing only recently left its infancy. There is a large variety of instruments and algorithms used for aerosol remote sensing. Aerosol products from TOMS (over land and ocean) and METEOSAT (over ocean only) turned out to be useful because of their long temporal series. New instruments, more specifically designed for aerosol retrievals, such as POLDER, MISR or MODIS, now provide more accurate measurements of aerosol optical depth. Some information is also available on the aerosol size distribution through the Angström coefficient or the relative weight of the accumulation and coarse modes. Aerosol retrieval over land surfaces is more difficult than over the ocean but progress has also been made. Using measurements of polarized light, POLDER can retrieve an aerosol index over land surfaces that may be interpreted as the optical depth of the aerosol accumulation mode [Deuzé *et al.*, 2001]. MODIS can retrieve the aerosol optical depth over land surfaces which are not too bright. Although these satellite aerosol products have been compared with ground-based measurements from sunphotometers, it is not clear how these measurements should be compared with each other and with model outputs. It will be particularly important to understand the exact nature of the satellite aerosol measurements made by the various instruments and reconcile the observed differences. Quite some attention should be given to potential biases that could arise from the satellite sampling and the cloud screening algorithm. Figure 3 shows the spatial and temporal scales involved in global-scale

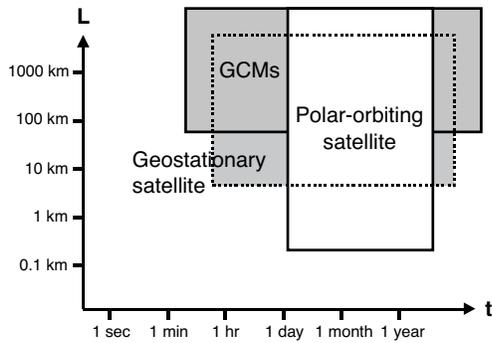


Figure 3. Spatial (L) and temporal (t) scales resolved explicitly in general circulation models (GCMs), geostationary and polar-orbiting satellites.

models, geostationary and sun-synchronous satellites. Comparisons between satellite observations and models (and *a fortiori* data assimilation) should consider the differences in scales, which can impact for instance the definition of clear sky. The scientific community (and the funding agencies) should progressively move from aerosol observation to aerosol monitoring.

## 4. The future

What should be the foci of future aerosol research to reduce the uncertainties in aerosol radiative forcings and climate feedbacks in which aerosols may be involved? It is, of course, not possible to give a complete answer. But, some research directions are clear. These include:

### Improving present and future emission inventories

This implies designing the emission inventories for anthropogenic aerosols in a way that makes it easy to update them. Future emissions of aerosols (on which the future climate depends to some extent) will be more influenced by the tolerance of people of their impacts on human health and ecosystems than by considerations of their impact on the climate! Therefore future emission inventories should incorporate social aspects in addition to economical ones. There is also a need to derive robust, physically-based parameterizations for natural aerosol sources.

### Focusing on the aerosol vertical profile

Surface and spaceborne passive instruments miss the vertical dimension of the aerosol distribution. However aerosol scavenging and transport and the direct effect in the longwave – which is important for mineral dust – depend critically on the vertical profile of aerosol properties. There is a large potential to improve models in this respect with the help of surface lidar networks (such as EARLINET) and the forthcoming spaceborne lidar missions (GLAS, CALIPSO, and EarthCare).

## Integrating scales using a hierarchy of models

There is a variety of spatial and temporal scales involved in aerosol measurements and modeling [Charlson, 2001]. Developing simple routine measurements worldwide and introducing data assimilation in global aerosol models can help get a global aerosol picture.

### Observing and modeling the state of mixture of multi-component aerosols

We should determine simple ways to describe and predict the hygroscopic and optical properties of the mixed aerosol from a limited number of parameters. Special attention should be given to the aerosol single scattering albedo, which is a critical parameter in aerosol radiative forcing.

### Distinguishing natural and anthropogenic contributions to the observed aerosol

It is not easy to separate the natural and anthropogenic components of the aerosol. Natural and anthropogenic material can even be mixed in a single particle. We should try, however, to see whether there are means to separate the natural and anthropogenic contributions to the aerosol using a combination of in-situ and remote observations.

### Studying the transition between clear and cloudy sky

Remote sensing tends to separate artificially clear-sky from cloudy-sky scenes and disregard partially cloudy scenes. For instance the POLDER algorithm considers 20% of the pixels being non-cloudy but not clear enough to perform an aerosol retrieval (this percentage depends critically on the spatial resolution, 6 km in the case of POLDER). In reality, we know that there can be a continuum between clear and cloudy skies, with situations of haze composed of aerosol droplets not activated but of micronic size [Charlson *et al.*, 2001].

### Developing a synergy between models and different satellite datasets

As mentioned above, this first requires an understanding of the effects of sampling and cloud screening in satellite data. Models and satellite data can be coupled through inversion and assimilation techniques. Model improvements should continue and satellite data should be used in more innovative ways. They can be useful to diagnose and monitor the regions of aerosol emissions. We should develop more original aerosol products, e.g. by deriving the aerosol radiative perturbation directly from the measurements of aerosol radiances or by combining aerosol retrievals from radiometers and radiation budget instruments (such as ERBE and CERES). Different satellite aerosol datasets can be merged together to develop level-4 aerosol products which combine the strengths of each dataset.

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## Appendix

Acronyms referred to in this article:

AERONET = Aerosol Robotic Network

CALIPSO = Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations

CERES = Clouds and the Earth's Radiant Energy System

EARLINET = European AeROSol Lidar NETwork

EarthCare = Earth Cloud, Aerosol and Radiation Explore

EMEFS = Eulerian Model Evaluation Field Study

EMEP = Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe

ERBE = Earth Radiation Budget Experiment

GLAS = Geoscience Laser Altimetry System

MISR = Multiangle Imaging SpectroRadiometer

MODIS=MODerate resolution Imaging Spectroradiometer

PHOTONS = PHOTométrie pour le Traitement Opérationnel de Normalisation Satellitaire

POLDER = Polarization and Directionality of the Earth's Reflectances

TOMS = Total Ozone Mapping Spectrometer

# Clouds, Atmospheric Chemistry and Climate

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## 1. Introduction

In agreement with the classical Köhler theory, clouds consist of “activated” droplets that grow spontaneously after they have reached a critical size, at a given supersaturation of the ambient water vapor. Hence, in theory, clouds are a well defined and separate atmospheric compartment with respect to wet unactivated particles and dry particles. Sometimes, however, what we see in the real atmosphere is different. This theoretical discontinuity is not perceived by the naked eye, nor by more sophisticated experimental tools, such as airborne or satellite-based instrumentation. To someone observing a fog over a polluted region, or clouds forming over biomass burning smoke, clouds are, in fact, a collection of drop-

lets, a continuum from ambient aerosol to wetter and wetter particles, to unactivated droplets, and then to activated ones. Moreover, “non activated” fog droplets with diameter smaller than the critical diameter for activation according to the Köhler theory have been observed in polluted conditions [Frank *et al.*, 1998].

In addition, being part of the complex atmospheric multiphase system (Figure 1), the atmospheric liquid phase (cloud droplets and wet aerosol) interacts with the gas phase and with the solid phase (dry aerosol, insoluble aerosol and ice crystals). A number of different chemical and physical processes cause exchange of mass between the different atmospheric reservoirs (the arrows between boxes in the figure). Chemical reactions in each compartment also occur (the “R” in each box), which change the chemical composition of the system [Fuzzi, 1994]. For example, a particle emitted by an anthropogenic or natural source, or produced by gaseous precursors, grows in the atmosphere as the relative humidity increases, eventually becoming a cloud droplet. This cycle, and all the physical and chemical processes occurring, depend on the state of the atmosphere (relative humidity, temperature, updraft velocity, etc.) and on the physical and chemical properties of the multiphase system in which the droplet forms (aerosol particle size and chemical composition, gas phase composition, etc.).

For this reason, the processes occurring in clouds cannot be studied in isolation from the entire multiphase system.

Cloud processes in the atmosphere also act on a wide variety of spatial (and therefore temporal) scales, varying from molecular processes acting on a spatial scale of a few Ångström (corresponding to a microsecond temporal scale), to synoptic meteorology characterized by a spatial scale of thousands of km (temporal scale of the order of days). This wide range of spatial and temporal scales involved in cloud processes (more than 15 orders of magnitude) is one of the main problems encountered in cloud modelling, since processes at the smallest scale cannot always be neglected in describing larger scale processes. A good example of this problem is the

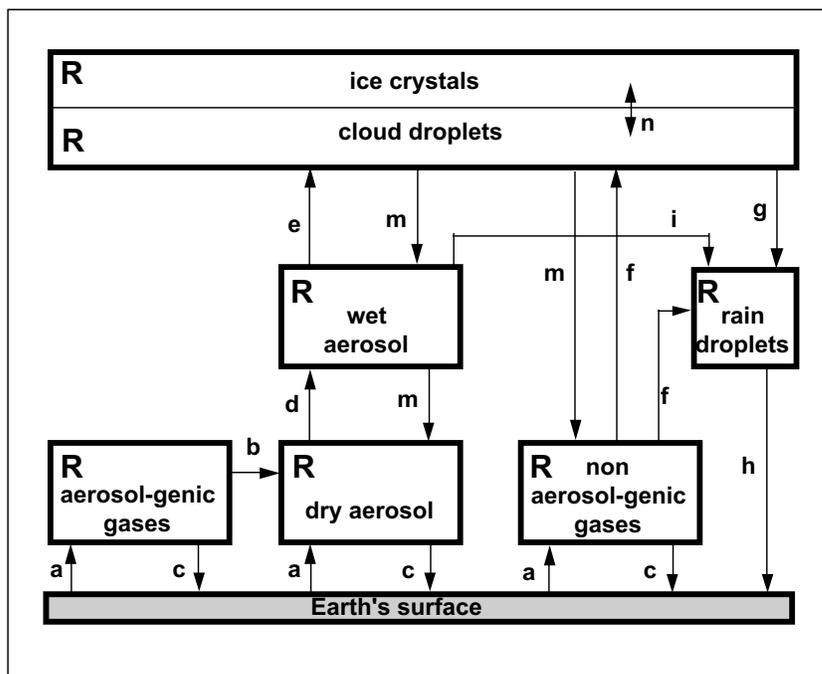


Figure 1. Graphic description of the multi-phase atmospheric system. Arrows represent physical and chemical processes leading to mass exchange between different phases. These include emission (a), gas-particle conversion (b), dry deposition (c), condensation (d), nucleation (e), dissolution (f), precipitation formation (g), wet deposition (h), aerosol capture by falling droplets (i),

prediction of cloud albedo variations due to changes in CCN concentration, which cannot simply be parameterized as a function of aerosol mass or aerosol number concentration, due to the variety of conditions observed in the real atmosphere [Schwartz and Slingo, 1996, Ramanathan *et al.*, 2001a].

## 2. Clouds in the atmosphere

Many important issues in atmospheric sciences involve clouds: aerosol physics and chemistry, gas phase chemistry, physics and chemistry of the ice phase.

Clouds interact with the aerosol population, causing a drastic depletion of the accumulation mode aerosol which, in turn, depends on the size and chemical composition of the CCN population itself. It is well known that soluble inorganic salts are efficient CCN, but organic compounds can also serve as CCN [Novakov and Penner, 1993]. Chemical reactions occurring in the liquid phase of clouds can also modify the composition of the droplets and, hence, of the aerosol population released into the atmosphere upon cloud dissipation.

Clouds also interact with gas phase chemistry: water soluble species like  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$ , low molecular weight organic acids and aldehydes are scavenged into the droplets during cloud formation and evolution, influencing the distribution between gas and liquid reservoirs, droplet chemistry, as well as the “oxidation state” of the entire multiphase system. Soluble radical species can be scavenged by clouds, thus affecting the oxidant budget within the droplets [Lelieveld and Crutzen, 1991; Liang and Jacob, 1997]. Not enough is known on the role of dissolved organic compounds and their interaction with transition metals in clouds. Knowledge in this field is far from allowing us to predict the effects of in-cloud transformations on global photochemistry [Ravishankara, 1997; Liang and Jacob, 1997].

In spite of the fact that most mid latitude clouds contain ice, the chemistry of the ice phase processes are almost unknown. A recent field experiment showed that the ice phase plays an important role in gas removal process, gases such as  $\text{H}_2\text{O}_2$  or  $\text{NH}_3$  being significantly adsorbed onto the ice crystals [Laj *et al.*, 2001]. There is also evidence that the  $\text{H}_2\text{O}_2$ - $\text{SO}_2$  reaction is much slower in the ice phase than in the aqueous phase. The influence of aerosol chemical composition on the ice nucleation process and, thus, on precipitation development has also recently been highlighted. Laboratory experiments showed that soot may be an efficient source of ice nuclei [Gorbunov *et al.*, 2001], and this may produce a *glaciation indirect effect* which could increase the efficiency of precipitation formation [Lohmann, 2002a]. This effect has an opposite sign with respect to the albedo indirect effect for warm clouds. The knowledge in this field is still at a rudimentary stage, and the study of the processes in iced and mixed-phase clouds are essential to predict the

cloud radiative effect and precipitation formation [Lohmann, 2002b].

There are several “indirect ways” that anthropogenic aerosol particles affect the Earth’s radiation balance and hydrologic cycle [Ramanathan *et al.*, 2001a]: they can enhance cloud reflectivity and hence cloud albedo, producing clouds with smaller but more numerous droplets [*first indirect effect*, Twomey, 1977]; they can change the efficiency of precipitation formation, causing a suppression of rain and enhancing cloud lifetime [*second indirect effect*, Albrecht, 1989]. Anthropogenic aerosols can also change the latent heat redistribution, possibly leading to changes in atmospheric circulation patterns. Aircraft measurements and more recent satellite observations have shown that these multiple facets of the indirect aerosol effect act on many different areas and in many different conditions. For example, satellite observations show a reduction of the effective radius, which causes a reduction of the precipitation efficiency over biomass burning areas, air pollution tracks and desert dust plumes [Rosenfeld, 1999; 2000; Rosenfeld *et al.*, 2001].

## 3. Influence of “chemical factors” on cloud formation and the role of aerosol organic compounds

The increase of the droplet number concentration is not a “simple” function of increasing aerosol number concentration as the recent INDOEX results show [Ramanathan *et al.*, 2001a,b]: the large degree of variation observed suggests that many different factors control cloud properties. Atmospheric parameters like moisture availability, updraft velocity temperature etc. are well known controlling factors, but aerosol properties (size distribution and chemical composition) are important as well. For many years, CCN chemical composition was assumed to be constituted only of inorganic soluble salts like  $\text{NaCl}$  or  $\text{NH}_4\text{SO}_4$ , and the Köhler theory, as it was initially formulated, considers only the inorganic aerosol; consequently, the parameterization of water activity is made for electrolytic aqueous solutions, which is not the case in the real atmosphere, where important quantities of organic compounds can be found in the aerosol. Recently, it has been shown that organic compounds and their properties (solubility, surface tension, etc.), as well as gas condensed within droplets (e.g.  $\text{HNO}_3$ ), are important “chemical factors” influencing cloud formation [Charlson *et al.*, 2001]. A recent paper on the water activity of organic-inorganic aqueous solutions shows how differently these complex mixtures should be treated with respect to aqueous inorganic solutions [Clegg *et al.*, 2001] but, at present, thermodynamic data for more realistic aerosol chemical compositions are not available.

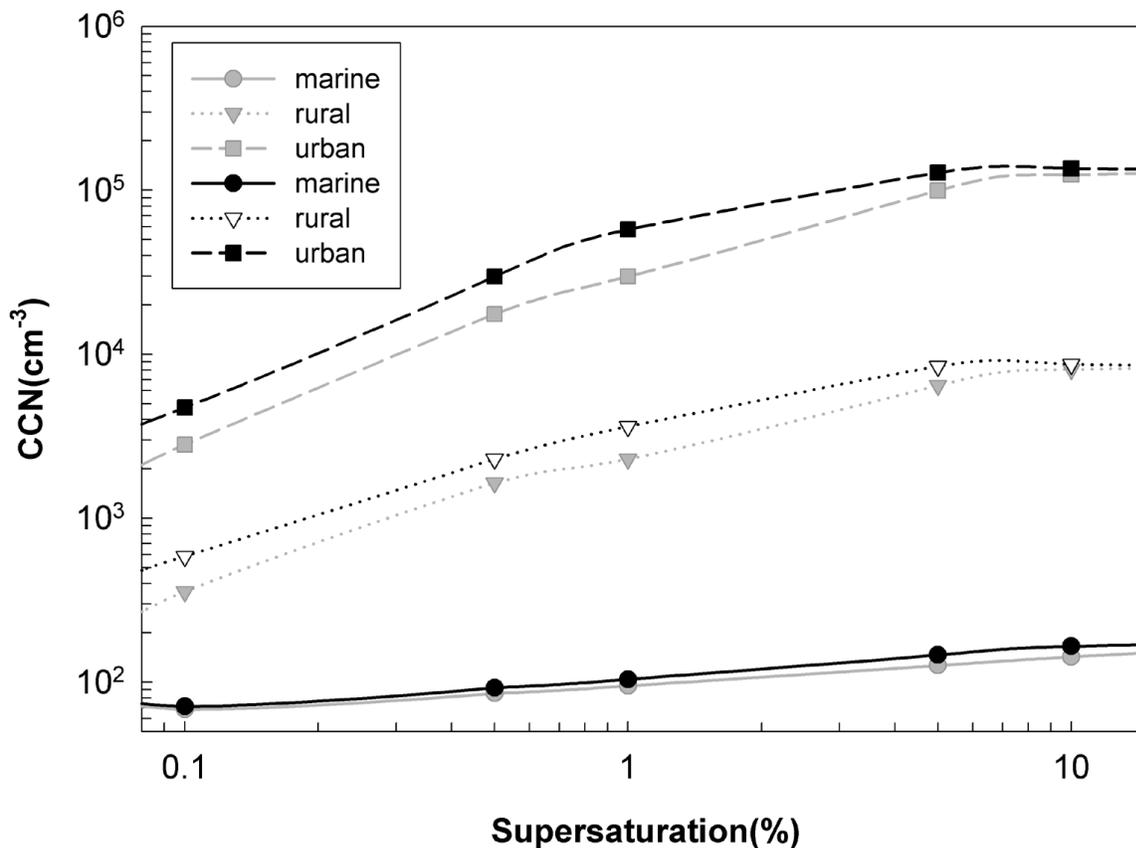


Figure 2. CCN concentration as a function of supersaturation for three aerosol types: marine (circles), rural (triangles), and urban (squares). The black lines include the presence of organic compounds, while the grey lines are computed including only the inorganic component [from Mircea *et al.*, 2002]

However, using a modified form of the Köhler theory [Shulman *et al.*, 1998], it has been shown that organic CCN influence cloud formation by “adding” soluble material in the droplet solution and by decreasing surface tension with respect to pure water [Shulman *et al.*, 1998; Facchini *et al.*, 1999; Mircea *et al.*, 2002]. Large reductions of the critical supersaturation were calculated, particularly in the case of small dry radius CCN [Mircea *et al.*, 2002]. In Figure 2, CCN supersaturation spectra are calculated considering different chemical compositions (both organic and inorganic) and typical size distributions derived from literature for a marine case, a rural case and an urban case. The increase in the CCN number concentration in the supersaturation range typical of real atmospheric conditions is significant in all three cases: up to 13% in the marine case, up to 97% in the rural case, and up to 110% in the polluted case [Mircea *et al.*, 2002]. This

sensitivity test shows the great importance of using meaningful chemical mixtures to simulate the inorganic and organic composition of real cloud systems: this is a major problem particularly in the case of organic compound, since only few, sparse measurements of the composition of the aerosol organic water soluble fraction (those compounds which most likely contribute to the CCN ability of particles) are available [Saxena and Hildemann, 1996]. Water soluble organic compounds (WSOC) represent a fraction ranging from 20% to 70% of the total aerosol organic carbon (OC), but on average only 5% or less of the WSOC mass can be attributed to specific compounds by means of traditional analytical techniques. For this reason, the properties of aerosol organic compounds are often simulated arbitrarily in current models, choosing compounds which have, in most cases, little contact with the physical reality.

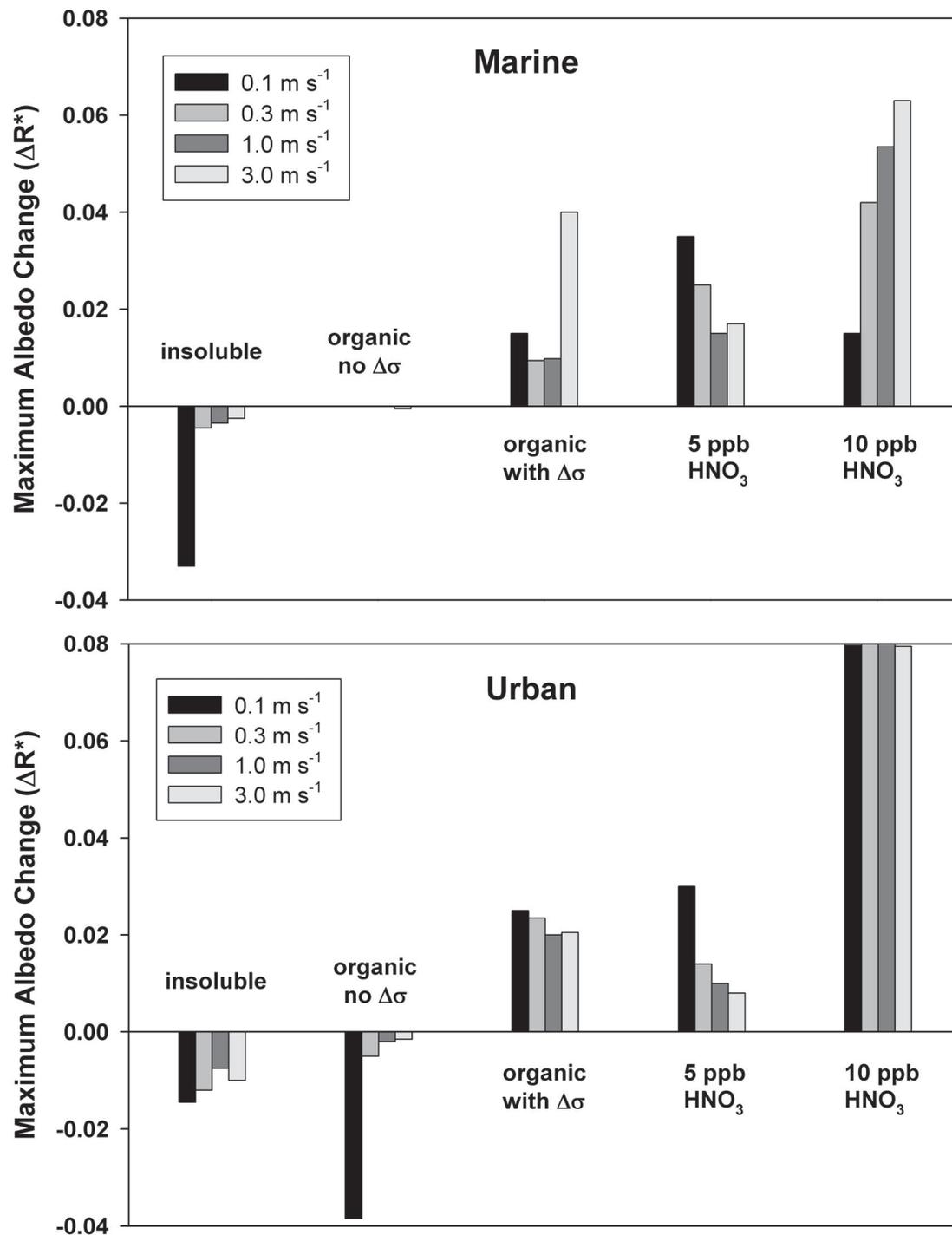


Figure 3. Maximum albedo difference, with respect to the baseline simulation, for a convective marine cloud and a convective urban cloud. Bar shading represents different updraft velocities. “insoluble”: CCN containing insoluble material (10% by mass for marine, 50% for urban); “organic no  $\Delta\sigma$ ”: CCN containing water soluble organic carbon (10% by mass for marine, 50% for urban) and no surface tension effects; “organic with  $\Delta\sigma$ ”: CCN containing water soluble organic carbon (10% by mass for marine, 50% for urban) and with surface tension effects; “5 ppb HNO<sub>3</sub>”: completely soluble inorganic aerosol with 5 ppb initial gas-phase HNO<sub>3</sub>; “10 ppb HNO<sub>3</sub>”: completely soluble inorganic aerosol with 10 ppb initial gas-phase HNO<sub>3</sub>. The organic fraction is assumed to be composed (by mass) of 18% levoglucosan, 41% succinic acid, and 41% fulvic acid.

Recently a new procedure has been proposed for deriving a simplified model of the water soluble organic fraction of the atmospheric aerosol [Fuzzi *et al.*, 2001]. Quantitative measurements of organic carbon concentration and proton concentration of the main functional groups contained in the aerosol WSOC mixture, measured by nuclear magnetic resonance [Decesari *et al.*, 2000], are used to formulate a set of a few *model compounds*, representative of the whole WSOC mass, which can be conveniently used to simulate in numerical models the physical and chemical properties of the organics dissolved in aerosols and clouds.

All of the above-mentioned “chemical factors” controlling cloud formation were introduced into an adiabatic cloud parcel model with detailed microphysics [Nenes *et al.*, 2001]. In this model, droplet form via condensational growth of the CCN population. A modified Köhler equation [Laaksonen *et al.*, 1998] was used to account for changes in the activation behavior of CCN due to the presence of surfactants, slightly soluble and insoluble compounds and condensable gas species. The results were compared with the effect of doubling the CCN concentration (Twomey effect). Cloud simulations relative to a baseline case in which cloud forms on CCN composed of purely inorganic salts shows how these factors affect cloud albedo (Figure 3). The magnitude of the cloud albedo variations observed depend on cloud dynamics (updraft velocity), as well as on the specific chemical CCN composition (marine and polluted case), and the model results generally show that the effects of the “chemical factors” are sometimes comparable to the Twomey effect of doubling the CCN concentration and may therefore be climatically significant. Unfortunately, it is currently impossible to calculate the global impact of all the variables influencing cloud formation, because adequate parameterizations of aerosol-cloud interactions for regional or global models are currently unavailable: only few, sparse data on aerosol organic composition exist and the theory for describing droplet growth at the fundamental level is still incomplete.

More broadly, the multiplicity of factors controlling critical supersaturation shade the border line between activated and non activated droplets, changing the traditional way of looking at clouds with a well defined distinction between wet aerosol and cloud droplets [Charlson *et al.*, 2001].

## 4. Chemical Reactions within cloud droplets

Another important issue in atmospheric chemistry concerns the in-cloud chemical transformations involving species derived from both the gas phase and aerosol. The picture is complicated by the fact that

cloud composition is size-dependent: pH can vary up to 2 pH units across the droplet spectrum, and variation in solute concentration up to a factor of 10 have been observed [Laj *et al.*, 1998]. This determines different extents of chemical reactions over the droplet spectrum. While several cloud models take this factor into account, the model validation is limited by the few measurements available of size-resolved cloud chemical composition [Collett *et al.*, 1995; Laj *et al.*, 1998].

Two main families of chemical species are key participants in liquid phase reactions: sulfur compounds and organic compounds. It is well known that S(IV) oxidation occurs at a much faster rate in clouds than in clean air, and global model results show that 80% of S(IV) to S(VI) oxidation in the atmosphere occurs in the liquid phase [Langner and Rodhe, 1991]. Many different pathways of oxidation have been studied and a few broad categories of S(IV) oxidation mechanisms by non radical species (e.g.  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ ), primary and secondary radicals (e.g.  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{NO}_3$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{SO}_x$ ,  $\text{Cl}/\text{Cl}_2$ ,  $\text{Br}/\text{Br}_2$ ,  $\text{CO}_3^-$ ), or reactions catalyzed by transition metals, are now reasonably well understood [Hermann *et al.*, 2001]. Conversely, organic chemical reactions in clouds are largely unknown and only C1-C2 species, mostly derived from the gas phase, are included in current models. However, evidence is available that solar irradiation of cloud water containing dissolved organic compounds produces  $\text{HO}_x$  radicals or  $\text{H}_2\text{O}_2$  [Anastasio *et al.*, 1997] but, at the same time, these organic soluble species may also act as a radical sink.

## 5. Future perspectives

Cloud chemistry and, more generally, the chemistry of aerosols is essential for the understanding of the climatic issues comprising indirect and direct aerosol effects. Cloud- aerosols processes, representing an important non-linearity in the climate system, are currently the most uncertain of the known climate forcings [IPCC, 2001]. The relationship between the forcings (e.g., changes in aerosol concentration and properties), effects (e.g. changes in cloud albedo, lifetime, extent, or precipitation development) and climate responses (e.g., changes in surface temperature or precipitation patterns and intensity) are currently very poorly understood .

Future research on atmospheric chemistry of the multiphase system including cloud should focus on the following primary topics.

### In-cloud organic photochemical reactions

Photochemical reactions of organic species dissolved in cloud should be investigated through laboratory

experiments (motivated by field experimental findings) to improve models, which currently contain only C1-C2 liquid phase reactions.

### Ice-phase chemistry

The present knowledge of cloud ice chemistry is at a rudimentary stage, but several studies have shown the potential impact of aerosol chemical composition on ice nucleation and on gas-ice equilibria. Field and laboratory research as well as thermodynamic modelling are needed to gain insight on this issue, and to formulate useful parameterization for global models.

### Aerosol and cloud chemical composition and related physico-chemical properties

Measurements of the size-segregated chemical composition of aerosols and cloud droplets (the organic fraction in particular) in different areas of the globe are urgently needed. In order to parameterize the complex organic-inorganic composition of aerosols and clouds for regional and global models, the organic composition should be simplified to a few model compounds representative of the whole organic mass. The main physical properties of aerosol (water activity, surface tension, solubility, density, freezing point) for different areas and different sources should also be determined.

### Relating models to observations

Laboratory and in-situ measurements of cloud and aerosol microphysics and chemistry, and of the main physico-chemical properties relevant to cloud formation should be combined with detailed cloud process modelling to obtain a better understanding of aerosol-cloud interactions and the related changes in cloud radiative properties. These models should be tested against observations, to identify the parameters and processes controlling cloud formation and development. In this respect, the coupling of ground-based observations to aircraft measurements, and to the new generation of satellite data through the models will be an important opportunity over the next decade.

### Bridging the scale gap

A major challenge for future research in the field of multiphase atmospheric chemistry is to bridge the gaps between the different spatial and temporal scales of cloud processes by both observations and modelling, in order to understand the impact of clouds on the Earth's radiation balance and the hydrologic cycle. A deeper comprehension of the microscale processes in all their facets is not, however, sufficient. Adequate parameterizations useful for large scale models

should be developed concurrently.

At the same time, the simplifications and parameterizations used in large scale models should be formulated in close contact with observations. For example, the first and second indirect effects of aerosols on climate are easily separated in a model framework, but cannot be disjointed by the observations [Boucher, 2002]. This paper also shows that the distinction between wet aerosol and cloud is sometimes difficult to observe in the real atmosphere. Therefore, it may be a problem to distinguish between direct and indirect effects in transition regimes between cloudy and clear sky. In order to obtain useful tools for interpreting and predicting climatic changes due to anthropogenic perturbations, a closer link between the experimental and modelling communities is of paramount importance.

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## Trace gas radiative forcings and related climate feedbacks: How do we reduce the uncertainties?

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### 1. Trace gas radiative forcings since the pre-industrial period

The abundance of many trace gases in the atmosphere is changing on local, regional, and global scales. We know that many of these changes are caused by anthropogenic emissions and related to energy production, transportation, industrial activities, land use, or agricultural practices. The radiative forcing due to all well-mixed greenhouse gas increase since pre-industrial times (1750) is estimated to be  $2.43 \text{ W m}^{-2}$  (including  $\text{CO}_2$  ( $1.46 \text{ W m}^{-2}$ ),  $\text{CH}_4$  ( $0.48 \text{ W m}^{-2}$ ),  $\text{N}_2\text{O}$  ( $0.15 \text{ W m}^{-2}$ ) and halocarbons ( $0.34 \text{ W m}^{-2}$ )) [Ramaswamy *et al.*, 2001]. The uncertainty on this direct forcing is 10 %. However, even if the level of scientific understanding of this forcing since the pre-industrial period is high, its past transient evolution, which reflects the spatial and temporal variability in the atmospheric concentration of greenhouse gases, is still complex to interpret. Figure 1 shows the growth rate of the long-lived greenhouse gas forcing from 1850 to present-day [Hansen and Sato, 2001]. This forcing shows a significant variability in time peaking at almost  $5 \text{ W m}^{-2}$  per century in 1980. The slowdown after this period is mainly caused by the phase-out of

ozone-depleting substances and by the observed recent flattening of the  $\text{CO}_2$  and  $\text{CH}_4$  growth rates. This trend in long-lived greenhouse gas concentrations and forcings clearly points towards the need for a better understanding of the magnitude and temporal evolution of their surface sources and sinks, and of their oxidation in the atmosphere which are mainly responsible for this recorded variability.

Ozone is also an important greenhouse gas which shows large spatial and temporal variability in both the troposphere and stratosphere. Tropospheric ozone changes contribute for  $0.35 \pm 0.15 \text{ W m}^{-2}$  (about 8-15%) to the total radiative forcing associated with greenhouse gas increase since the pre-industrial. This estimate is based on a large range of model studies and on an analysis constrained by observations [Kiehl *et al.*, 1999]. The main uncertainty on this forcing arises from the limited information on pre-industrial  $\text{O}_3$  levels. Recent studies reexamined this forcing and the assumptions made on ozone at the beginning of the nineteenth century, and calculated a forcing larger than  $0.7 \text{ W m}^{-2}$  [Mickley *et al.*, 2001; Hauglustaine and Brasseur, 2001]. Comparison of model results with surface ozone measurements recorded during the 19th century (and subject to very limited confidence) are generally consistent at mid-latitudes over Europe, showing mixing ratios of about 10 ppbv, with little variation throughout the year. The situation is more complex in tropical regions where recorded pre-industrial ozone levels at the surface indicate very low values of only 5 ppbv. The calculated pre-industrial ozone levels appear very sensitive to the assumptions made for natural emissions of NO (soils, lightning) and hydrocarbons, and for biomass burning emissions.

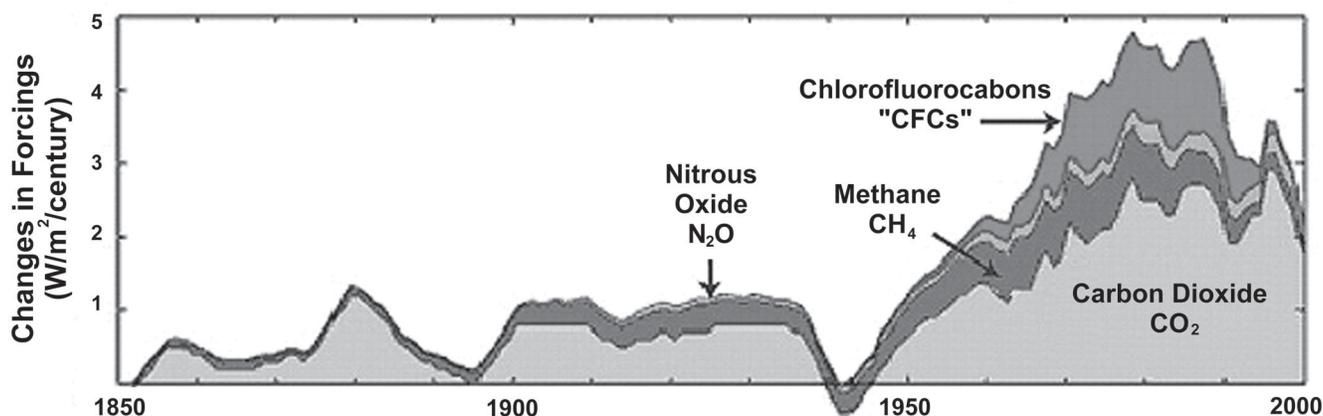


Figure 1. Growth rate of radiative climate forcings by well mixed greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , CFCs) (from Hansen and Sato, 2001).

## 2. Indirect forcings and feedbacks and their evolution into the 21st century

In addition to the direct forcings caused by the injection of radiatively active gases to the atmosphere, the concentration and distribution of radiatively active gases can also be indirectly modified by the emission of gases that influence their production or destruction in the atmosphere through chemical transformation. Because of the central role of O<sub>3</sub> and OH in tropospheric chemistry, the chemistry of CH<sub>4</sub>, CO, NMHCs, and NO<sub>x</sub> is strongly intertwined, making the interpretation of the responses to emission changes rather complex. The uncertainties connected with estimates of these indirect effects are much larger than the uncertainties of those connected to estimates of the direct effects.

Due to their localized emissions and short lifetimes, reactive chemical species have inhomogeneous distributions in the atmosphere. This is particularly the case for nitrogen species which exhibit a distribution highly variable in space and time. Due to non-linearities in ozone photochemical production together with differences in mixing regimes and removal processes, the O<sub>3</sub> perturbation strongly depends on the location of the ozone precursor emission (CO, NMHCs, NO<sub>x</sub>). Figure 2, shows that the tropospheric ozone radiative forcing associated with a 40 Tg increase in CO emission is 10-20 % larger when this emission is applied in the tropics (i.e., SE Asia) rather than at mid-latitudes (i.e., western Europe). In the case of a 1 Tg-N increase in NO<sub>x</sub> surface emission, the calculated forcing is found to be 6-8 times larger for a perturbation localized in the tropics. As discussed by Fuglestad *et al.* [1999] and Wild *et al.* [2001], for the NO<sub>x</sub> emission perturbation scenario a negative indirect forcing, which partly offsets the ozone forcing, also arises from the increased OH concentration and the resulting shorter CH<sub>4</sub> residence time in the atmosphere. These indirect forcings involving ozone and OH clearly show that the geographical location of the emission appears to be of crucial importance.

The altitude of the perturbation also appears to be a key factor as far as radiative forcings and their climate response are concerned. It has been shown previously [e.g., Forster and Shine, 1997], that, similarly to water vapor, the climate response is sensitive to the altitude at which an ozone perturbation occurs (Figure 3), and that it is most sensitive to a perturbation to ozone number density in the tropopause region. However, unlike water vapor, the ozone concentration peaks in the stratosphere and so the climate response to a percent perturbation extends throughout the lower stratosphere. This suggests that the sensitivity of climate to the altitude of O<sub>3</sub> perturbations is smaller than suggested by earlier studies that employed constant absolute changes to investigate these effects. The upper-troposphere and

lower-stratosphere (UTLS) is still considered as a key region of the atmosphere as far as composition and climate interactions are concerned for the following reasons:

- Radiative forcing by greenhouse gases such as water vapor and ozone remains especially sensitive in the UTLS to concentration changes, due to large temperature contrast with the surface.
- The UTLS is the layer in which stratospheric and tropospheric air are mixed. The exchange between these atmospheric domains controls the influx of tracers into the stratosphere (including water vapor and long-lived greenhouse gases), and the O<sub>3</sub> and NO<sub>x</sub> flux from the stratospheric reservoir down into the troposphere.
- Chemistry in the lower stratosphere is very sensitive to temperature changes and, at high latitudes, to the presence of Polar Stratospheric Clouds (PSCs). Stratospheric ozone concentration and temperature changes are directly coupled providing an important climate-chemistry interaction. The UTLS also coincide with the height of transition between positive and negative trends as detected by ozone sondes.
- Due to the influence of rapid convection within cloud structures and the large-scale vertical transport associated with convergence, the imprints of lower tropospheric events such as biomass burning and forest fires and several regional air pollution episodes are also imposed on the upper troposphere.
- In this relatively dry region, species like peroxides and oxygenated hydrocarbons play a major role in controlling the budget of HO<sub>x</sub> radicals. Heterogeneous chemical reactions on cirrus clouds may also affect the budget of ozone and other species at these altitudes.

Emissions of ozone precursors are expected to increase significantly in the future. This is particularly the case in regions where rapid economic growth or population increase are expected (e.g., Southeast Asia, South and Central America, Africa). These regions also coincide with the highest sensitivity of ozone to its main precursors as illustrated above. Estimates of future levels of tropospheric ozone and associated radiative forcing have been performed with several chemical-transport models and under various assumptions regarding the future evolution of precursor emissions. Very recently, an extensive modeling study has been conducted by Prather *et al.* [2001]. This study is based on the IPCC SRES future emission scenarios for the 2100 time horizon and involved 11 global chemical-transport models [Gauss *et al.*, 2002]. Despite the large variations in future ozone levels and associated forcings predicted by the participating models (and mainly associated with

differences in model physics and chemistry), several salient features appear. In particular, in all models, a maximum increase in ozone tropospheric column is predicted in 2100 over the tropical regions. All models also converge in calculating a maximum ozone response in the upper troposphere, precisely where the impact on climate is the largest.

This OxComp inter-comparison exercise also indicates that the various assumptions made on the magnitude and location of future emissions of precursors induce a larger spread in the results than inter-model differences. As discussed by Wigley *et al.* [2002], it is also very important to note that for reactive gases, the SRES scenarios used for global climate simulations do not incorporate local air quality issues. As a consequence, it is likely that these future simulations will imply high urban ozone levels (in particular in mega-cities) unacceptable based on air quality considerations. For sake of realism, the

scenarios of future emission levels of reactive gases (and particles) will have to account for deterioration of air quality and clean air treaties.

The large seasonal and inter-model ranges obtained for the tropospheric ozone radiative forcings since the pre-industrial and in 2100 for the OxComp exercise compress somewhat when normalized forcings are considered (forcing per tropospheric ozone column increase). For the sensitivity simulations illustrated in Figure 2, for the evolution since the pre-industrial [Hauglustaine and Brasseur, 2001], and in 2100 [Gauss *et al.*, 2002], normalized forcings of respectively 45, 41, and 36  $\text{mW m}^{-2} \text{DU}^{-1}$  are obtained when averaged among all participating models. Mickley *et al.* [1999] have demonstrated that this normalized forcing at extra-tropical latitudes is largely determined by the temperature difference between the tropopause and the surface, while cloud cover plays a dominant role in the tropics. This suggests that the dif-

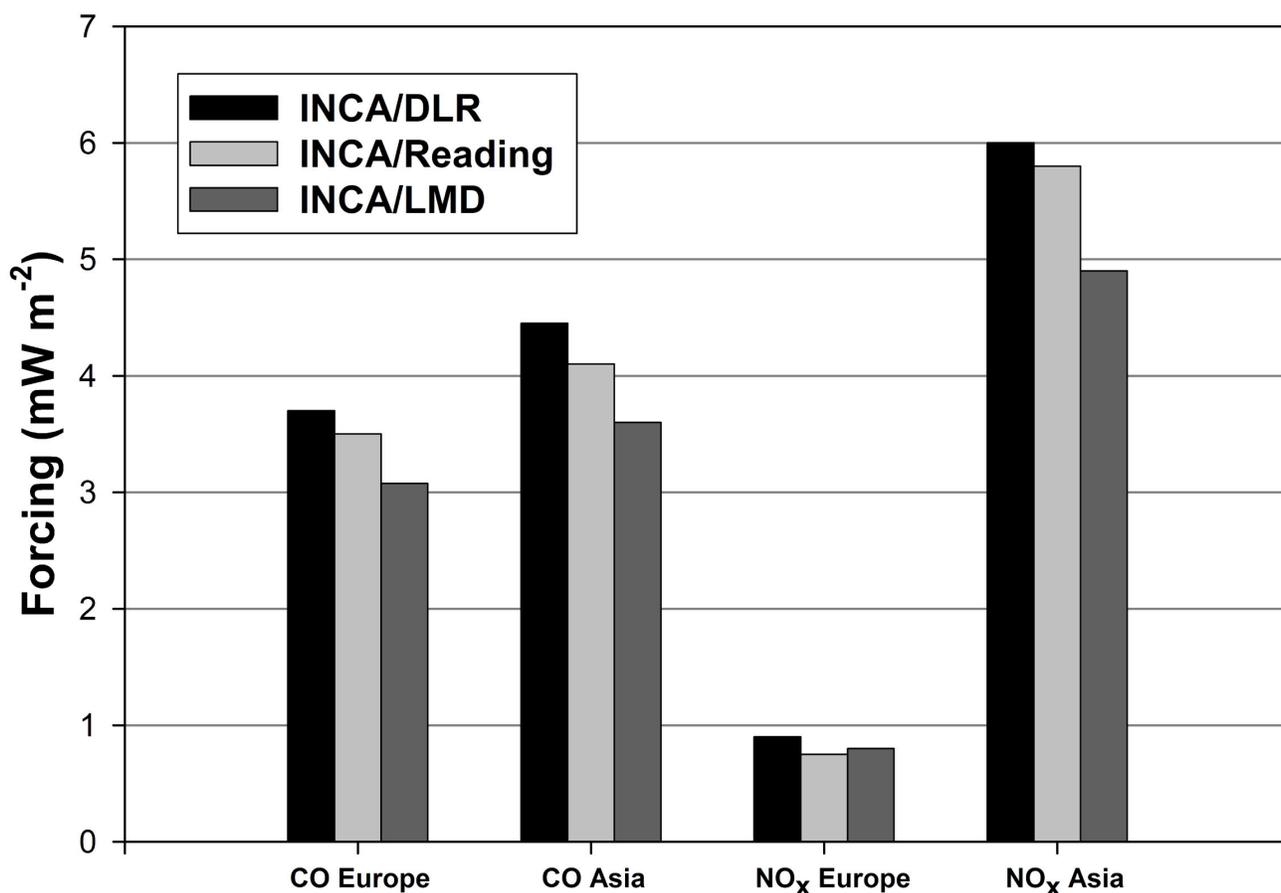


Figure 2. Tropospheric ozone radiative forcings associated with an imposed 40 Tg increase in CO or a 1 Tg-N increase in NO<sub>x</sub> surface emissions applied in Europe or Southeast Asia ( $\text{mW m}^{-2}$ ). The chemical perturbations are calculated with the LMDzT-INCA climate-chemistry model and the associated radiative forcings are calculated with the radiative transfer models from DLR, the University of Reading, and LMD. Similar calculations have also been performed with the University of Oslo chemical-transport model in the framework of the METRIC EU project [Berntsen *et al.*, 2002]

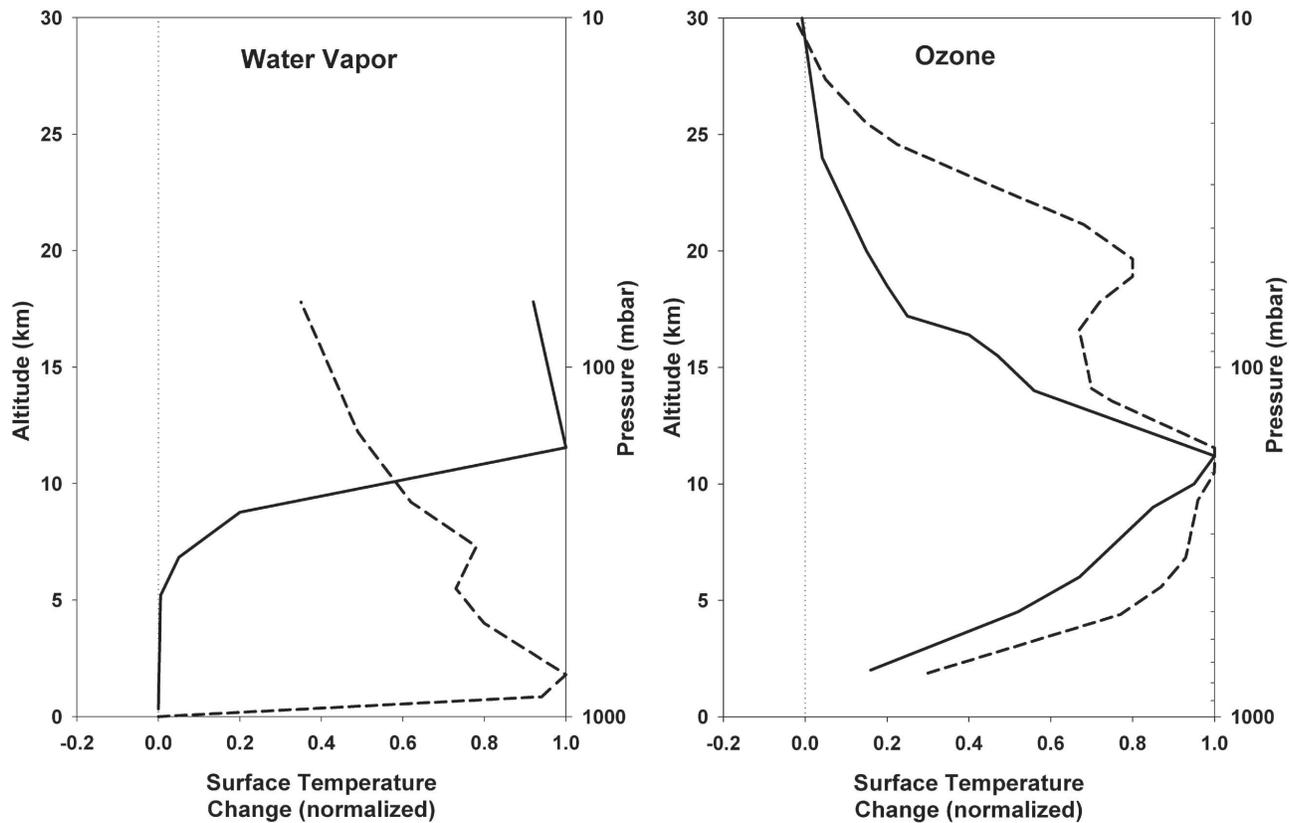


Figure 3. Surface temperature responses to perturbations in water vapor and ozone as a function of height as calculated by a radiative-convective climate model. The curves present normalized surface temperature responses to both a fixed increment in number density (solid line) and a fixed percentage increment (dashed line). Adapted from Shine and Sinha [1991] and Forster and Shine [1997] (courtesy of B. Kerridge).

ferences in physical climatology between models, and their comparison to the real atmosphere play a key role in these calculations. The background ozone in the model is also a major source of uncertainty as illustrated by the difference obtained in the normalized forcings for the pre-industrial and 2100 simulations, and by the difference obtained when the normalized forcings are calculated for the tropics or for the northern and southern hemisphere separately.

Water vapor is the major contributor to the natural greenhouse effect and the main source of radicals in most of the troposphere. The  $H_2O$  distribution is governed largely by dynamics and thermodynamics, allowing feedback with temperature changes due to other greenhouse gases. The magnitude of the water vapor and cloud climate feedbacks is a major uncertainty in climate models. The chemistry of the troposphere is directly influenced by the changes in humidity and temperature. These couplings provide feedbacks between climate change induced by in-

creasing greenhouse gases and the chemical processing of trace gases. These feedbacks of humidity and temperature can actually amplify or damp the chemical response as identified by Brasseur *et al.* [1998], Stevenson *et al.* [2000], or Johnson *et al.* [2001]. Furthermore, the continental and oceanic biosphere response to global change will also impact on atmospheric composition. The changes in climate (e.g., temperature, humidity, precipitation), in carbon dioxide concentration, and in chemistry will alter ecosystems and consequently natural emissions of trace gases as biogenic hydrocarbons or the removal of chemical species by dry deposition [Constable *et al.*, 1999; Petron *et al.*, 2001]. These changes in climate and in biogenic emissions provide additional feedbacks which affect both the oxidizing efficiency of the atmosphere and the budget of greenhouse gases. They add further indirect radiative perturbations to the Earth system which are difficult to quantify and hence subject to large uncertainties.

### 3. The need for carefully evaluated coupled climate-chemistry models

Current chemical-transport models of the atmosphere typically include 50-100 chemical compounds and 100-300 (photo-)chemical reactions and are run on a typical 2 degree by 2 degree resolution with 20-60 vertical levels. These models have been used in various inter-comparison exercises and evaluations against large-scale campaigns as the various NASA GTE campaigns [e.g., Emmons *et al.*, 2000] or measurements made on-board commercial aircraft as MOZAIC, NOXAR, and CARIBIC [e.g., Law *et al.*, 2000; Brunner *et al.*, 2001]. These exercises have indicated that the models reproduce with reasonable success the global behavior of the distribution of ozone and its precursors in the atmosphere. Severe differences and bias also appear and will need to be addressed in more detail in the near future in order to improve simulation of the atmospheric composition evolution and its role in the climate system.

To better investigate the interactions between chemistry and climate, it appears crucial that the next model generation includes both tropospheric and stratospheric chemistry. The need to treat simultaneously both systems is essential in order to understand and try to reproduce the observed trend in ozone in the troposphere and in particular in the UTLS region. Many indirect climate forcings, associated for example with stratospheric water vapor increase or increased penetration of UV radiation into the troposphere and subsequent impact on the oxidizing efficiency, will only be adequately represented if both the troposphere and the stratosphere are correctly accounted for in the models. Such models are currently under development or have already been used with simplified tropospheric chemistry in order to investigate for instance the impact of aircraft emissions on the composition of the atmosphere. In the future, they will be further improved in order to include more detailed representations of tropospheric processes including non-methane hydrocarbon chemistry and surface processes.

An important objective of the modeling community will also be to develop and apply coupled chemistry-climate models. It is only recently that general circulation models have been fully coupled to chemical processes, and the first studies performed with these models provide exciting new insights on how the coupled climate system amplifies or damps the chemical perturbations. Simulated impact of climate changes on the oxidizing efficiency of the atmosphere through perturbation of humidity, temperature, unresolved transport as convection (including scavenging of soluble species and lightning NO<sub>x</sub> emissions), or cloud distribution clearly emphasizes the need for

fully coupled models. This is further reinforced by recent findings showing clear connection between ozone and the climate variability and oscillations as ENSO or NAO. These models will have to be further refined in the future in order to include more detailed chemistry, the coupling with the stratosphere as well as interactive emissions from the biosphere.

The coupling between these complex models (atmosphere, ocean, biosphere, carbon cycle, chemistry and aerosols) probably constitutes the way forward to identify and better quantify the indirect climate forcings associated with chemistry. However, the sources of uncertainty in the estimate of these forcings will also increase together with the complexity of the models. In order to reduce these uncertainties on the radiative forcings associated with chemistry these models have to be carefully evaluated. This evaluation is requested not only for chemical species but has to be performed simultaneously for physical, dynamical, chemical, and biospheric processes. This will require not only large-scale campaigns which investigate the inter-continental transport of pollutants but also campaigns focusing on a given region or on specific processes poorly understood and represented in the models. The emphasis of these campaigns will be on the coupling between chemistry-aerosols, emissions, and climate.

Observations from space are essential to evaluate the models because they provide a unique global perspective and uniform sampling of constituents which vary both spatially and temporally. In the troposphere, recent observations of O<sub>3</sub>, NO<sub>2</sub>, and CH<sub>2</sub>O tropospheric columns from GOME/ERS-2, and of CO from MOPITT/EOS-Terra have provided unique and new evidence of the large-scale perturbation of the atmospheric composition by human activities. These datasets are now complemented by the observations of chemical species in the troposphere by SCIAMACHY/Envisat and soon by OMI and TES onboard EOS-Aura. In order to fully meet the stringent measurement requirements imposed by the climate-chemistry studies, future space missions will have to be further optimized to probe down into the troposphere. In particular, this includes a high horizontal resolution to address pollution related issues, information on the vertical distribution of species (and more specifically in the UTLS where sharp vertical gradients exist), information on the diurnal variation of chemical species, and new species of interest for tropospheric studies. This should be undertaken simultaneously with the monitoring from space of active fires and of lightning flashes to impose further constraint on the models and on the emission of ozone precursors.

Data assimilation provides an intelligent means to interpolate observations in time and space; to integrate

diverse elements of large measurement and modeling programs and to combine, inter-compare, and characterize the observations from different types of instruments. Inverse modeling and chemical data assimilation techniques are advancing rapidly and are expected to reach a high level of sophistication in the near future. These techniques will for example allow to infer the distributions of species that are not observed directly by satellite, which interact chemically with observed species. They will also allow to fully take advantage of satellite and network observations to improve the emission inventories of source gases.

## 4. Conclusions

The uncertainties in the calculation of trace gas radiative forcings of climate arise from our limited understanding of the global distribution, budget and evolution of greenhouse gases in the atmosphere. The budget of key species is governed by their emissions at the surface and sink in the atmosphere (or at the surface). Natural emissions are responsible for a large part of the observed variability of long-lived greenhouse gases and ozone precursors as  $\text{NO}_x$  and NMHCs. The magnitude of these emissions, their distribution and response to climate change is a major source of uncertainty.

The oxidizing efficiency of the atmosphere (referring mainly to the level of OH but also of other oxidants such as  $\text{O}_3$ ,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$  or  $\text{NO}_3$ ), which controls the residence time of most of the greenhouse gases and other pollutants, is the other crucial parameter [e.g., Lawrence *et al.*, 2001]. It is controlled primarily by water vapor, exchanges between the troposphere and the stratosphere, penetration of UV radiation, aerosols, and its past evolution. Future changes in the oxidizing efficiency of the atmosphere remain very uncertain.

These two major uncertainties clearly point to the need to further develop and apply fully coupled models accounting for the various and complex interactions between the atmosphere, the ocean and the continental biosphere from a physical, chemical and biological point of view. In addition to that, in order to really address the indirect forcings associated with chemistry, these models should include not only the gas phase chemistry in the troposphere and stratosphere but also the role played by aerosols on photolysis rates and as active chemical sites.

These coupled models will have to be carefully evaluated before a reasonable confidence can be achieved in terms of radiative forcings and climate feedback calculations. The various components of these models already exist with different levels of complexity in their representation of physical and chemical processes. The major challenge of the community will not

only be in the coupling and improvement of the various components of Earth system models but also in the careful evaluation of the simulated climate, composition, and their coupled evolution. This can only be attained through a synergistic use of space-based observations, ground-based networks and dedicated large-field campaigns.

A further difficulty arises from the fact that the radiative forcing concept was originally formulated for the global and annual mean climate system. It has been extended to smaller spatial domains, and smaller time-averaging periods in order to deal with short-lived species that have a distinct geographical and seasonal character such as ozone or other indirect forcings. An important question is whether the inhomogeneous forcings have climate sensitivities similar to forcings from long-lived greenhouse gases. Several recent studies have already shown that it is certainly not the case and that the climate sensitivity is quite dependent on the altitude and geographical distribution of the applied forcing agent.

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## IGAC *tivities* Newsletter

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## Announcements

### Atmospheric Chemistry within the Earth System: From Regional Pollution to Global Change

10th Scientific Conference of the CACGP and 7th Scientific Conference of the IGAC

18-25 September 2002

Creta Maris, Hersonissos, Heraklion, Crete, GREECE

#### Observing our changing atmosphere

Distributions and trends of radiatively and chemically active substances, The view from space (gases, aerosols, clouds, radiation)

*Invited Contributors:* A. Thompson, F. Raes, D. Rosenfeld, J. Burrows, J. Fishman

#### Impacts

Radiative forcing/chemistry-climate interactions, Element cycle interactions, Nutrient mobilization, redistribution, fertilization, and other impacts

*Invited Contributors:* J. H. Seinfeld, R. Duce, J. Galloway

#### Atmospheric composition change: Processes and mechanisms

New radical chemistry, Multiphase chemistry, Upper troposphere-lower stratosphere interactions, Aerosol/cloud/radiative processes and interactions, Atmosphere-surface exchanges

*Invited Contributors:* U. Platt, M.C. Facchini, A. Cox, P. Quinn

#### Major campaigns with regional focus

Mediterranean area, India, Asia, Pacific, Amazonia, Africa and others

*Invited Contributors:* J. Lelieveld, V. Ramanathan, B. Huebert, D. Jacob, P. Artaxo, H. Annegarn

#### 'Hot' Topic Short Sessions

- Stability of global OH and detection of OH trends - R. Prinn, P. J. Crutzen
- New particle formation: How and where does it happen? - Th. Hoffmann, M. Kulmala
- Optimally confronting model results and satellite observations - O. Boucher, C. Granier
- Large scale/hemispheric scale air pollution - S. Penkett
- The importance of controlling short-lived greenhouse gases/aerosols versus CO<sub>2</sub> in alleviating global warming - V. Ramanathan, M. Heimann
- The role of the biosphere in climate change - P. Matson

#### Open Meetings

18 Sept.: IGAC in its second decade: Plans for a follow-up program

23 Sept.: CACGP activities

**Hotel Reservation deadline: June 30, 2002**

**E-mail: [info@grecomar.gr](mailto:info@grecomar.gr)**

#### Registration Fees:

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350 Euro (students: 250 Euro)

Payment after June 30, 2002:

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## **IGAC** *tivities* Newsletter

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